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SURFACE MODIFICATION, ORGANOMETALLIC AND POLYARYL POLYMER COATINGS,
AND FLAME SPRAY TECHNOLOGIES FOR PREVENTING CORROSION OF METALS

Final Report

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ABSTRACT

To improve adherent properties of electrogalvanized steel (EGS) to polymeric topcoats, the surfaces of EGS were modified by polyelectrolyte-modified zinc phosphating solution. The electrochemical reaction between phosphating solution and EGS led to the complete coverage with fully grown hopeite crystals after only 5 sec treatment, thereby improving adhesion to topcoating and providing protection of EGS against corrosion. To evaluate the ability of polyphenylene sulfide (PPS) polyaryl thermoplastic coatings to protect zinc phosphate (Zn•Ph)-treated steels from corrosion in a wet, harsh environment (1.0 wt% H_2SO_4 , 3.0 wt% NaCl and 96.0 wt% water at temperatures from 25° to 200°C), we exposed them in an autoclave to attempt heating-cooling cyclic fatigue tests (1 cycle = 12 hr at 200°C + 12 hr at 25°C) up to 90 times. The major chemical reaction at the interface between the PPS and Zn in the Zn•Ph layer during cycling led to the formation of ZnS reaction product, which enhanced the Zn•Ph-to-PPS adhesive bond; correspondingly, there were no signs of peeling and separation of the coating after 90 cycles. Organometallosiloxane polymer (OMSP) was synthesized through the hydrolysis-condensation reaction of the mixed precursor solutions of the N-[3-(triethoxysilyl)propyl]-4,5,-dihydroimidazole and β -trimethoxysilylethyl-2-pyridine sols in liquor medium and the metal alkoxides and metallocene dichloride dissolved in water or tetrahydrofurane. The OMSP films (thickness, 0.5 to 1.0 μm) deposited by simple dip-withdrawing coating methods to aluminum alloys displayed the impedance of $> 10^6$ ohm-cm² after exposure for 40 days in 0.5 N NaCl solution at 25°C and the 3000 hr-salt spray resistance. Using a flame spray coating process, the methacrylic acid-modified polyethylene copolymer was overlaid onto cold rolled steel surfaces. An appropriate setting of the rate of air flow led to the incorporation of increased numbers of functional oxygen derivatives, such as COOH and C=O groups, into the copolymer, thereby, improving the interfacial bond strength of the copolymer-to-steel joints.

STATEMENT OF WORK

Under U.S. Army Research Office (ARO) sponsorship, on Contract Numbers, MIPR-ARO 157-92, 112-93, 102-94, and 117-95, Brookhaven National Laboratory (BNL) performed research on four topics:

- 1) Surface modification of electrogalvanized steels,
- 2) High-protective performance polyaryl coating systems,
- 3) Synthesis and characteristics of organometallic polymer coating films, and
- 4) Organic polymer coatings by flame spray technology.

Major research activities within each of these topics are described below.

1. Surface Modification of Electrogalvanized Steels

In the automotive industry, it is commonly known that electroplated coatings of pure zinc and various zinc alloys over steel surfaces are responsible for improving corrosion resistance by delaying the onset of "red rust" of body panels and various discrete parts, such as fasteners and brackets [1]. Pure zinc coatings currently have the major share of the automotive body-panel market. Although the art of making electroplated zinc coatings for electrogalvanized coatings is well developed, two problem areas still remain. One problem is the poor adherent property of galvanized (Zn) coating surfaces to the polymeric topcoats, and the other is the necessity of post-treatment to inhibit the onset of "white rust", which represents deterioration of the zinc layer. The former problem relating to the paint's adhesion properties is due primarily to the chemically inert, smooth texture of coating surfaces. One method to solve this problem is to increase the roughness of the surface either by etching or by sandblasting [2]. Such roughening procedures, which increase the actual surface area, provide more mechanical interlocking bonds at interfaces between the paint and the Zn coating. However, there is no resolution to inhibiting the onset of "white rust" of Zn coatings.

Thus, our research focused on modifying Zn coating surfaces to improve their chemical and physical affinities with paint, and retard the corrosion rate of Zn layers. Poly(acrylic acid), p(AA),-incorporated zinc phosphate solutions were used for this work. As discussed in our previous papers [3,4], crystalline zinc phosphate (Zn•Ph) conversion coatings can be prepared by immersing cold-rolled

steel into a p(AA)-incorporated phosphating solution. The Zn•Ph coating deposited on the steel surfaces not only served to protect the underlying steel against corrosion, but also had excellent adherent properties to paint. The latter contribution was due mainly to the combined effects of the very rough surfaces of Zn•Ph and the strong chemical affinities of p(AA) macromolecule existing at the topsurface of the Zn•Ph layer. Our particular interests were to investigate and explore how this phosphating solution is converted into solid Zn•Ph layers adhering to the underlying Zn coating, and how well the polymeric topcoat will bond to them.

2. High-Protective Performance Polyaryl Coating Systems

Crystalline polyphenyletheretherketone (PEEK) and polyphenylene sulphide (PPS) thermoplastics are very attractive as corrosion-protective coatings for cold-rolled steels in harsh environments at hydrothermal temperatures up to 200°C. The major characteristic of these linear polyaryls is their molecular orientation caused by chain extension at a melting point of $\approx 290^{\circ}\text{C}$ for PPS [5,6] and of $\approx 340^{\circ}\text{C}$ for PEEK [7,8]. This orientation causes the crystallization of these polymers during cooling. Such melt-crystallization behaviors of these polyaryls give them specific, desirable characteristics as coatings, such as high-temperature stability, chemical and hydrothermal resistance, and good mechanical properties.

In our previous studies on the adhesive properties of polyaryls to steel surfaces, we found that the bond strength of the PPS-to-steel joints prepared in an air or in an oxygen-free N_2 gas environments depends on the species of sulphur-related iron compounds formed by the chemical reaction between the SO_2 gases emitted from PPS and Fe_2O_3 at the outermost surface sides of the steel, but is independent of the degree of crystallinity of PPS adjacent to steel [9]. This finding suggested that the formation of oxygen-catalyzed reaction compounds resulting from the introduction of oxygen into the interfacial regions gave better adhesion than bond structures assembled in N_2 gas. In contrast, in PEEK/steel joints, the incorporation of oxygen into the interfacial boundary regions not only promotes the nucleation of crystalline PEEK caused by extensive oxidation of steel interface, but also affects the oxygen-catalyzed decomposition

of PEEK, thereby resulting in its separation from the steel [10]. When this system was prepared in N₂ gas, it exhibited good bonding, because of the charge transfer reaction between PEEK and steel, and the formation of a well-crystallized PEEK.

On the other hand, an ideal polymeric coating that will protect steel from corrosion is one that acts as a barrier against the attack of corrosive reactants, such as oxygen, water, electrolyte species (e.g., H⁺, Na⁺, Ca²⁺, NH₄⁺, Cl⁻, SO₄²⁻, NO₂⁻) and gases (e.g., O₃, SO₂, NO_x), in natural or artificial environments. Unfortunately, these reactants are permeable to all polymeric coatings in some different degrees. Thus, an important consideration is that when the reactants reach the steel surfaces beneath the coating layers, corrosion occurs at the interfaces between polymer and steel. Once corrosion is initiated, the growth of corrosion products at the interfaces promotes wedging and blistering which puts tremendous stress on the interfacial side of coating film; consequently, there is localized delamination and buckling of the stressed coating layers [11]. In addition, if the coating films become blemished, the underlying steels react with the reactants that have penetrated through the defect. Such a reaction is commonly called the two-step corrosion reaction: a cathodic reaction, $\text{H}_2\text{O} + 1/2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$, which occurs under the coating, and an anodic reaction, $\text{Fe} - 2\text{e}^- \rightarrow \text{Fe}^{2+}$, which occurs at a defect in the coating [12,13]. Considerable attention in this corrosion process has been given to the low pH environment created at the cathodic sites; namely, the alkali generated beneath the coating not only causes the formation of corrosion products, but also promotes the saponification of the polymer adjacent to the steel [14-16]. Subsequently, these phenomena occurring at the interfaces between the polymeric coatings and the steels lead to the cathodic delamination of the coatings from the steels. Thus, it is very important to tailor and modify the interface to inhibit the onset of the cathodic reaction.

For such tailoring of material systems for auto body applications, zinc or zinc alloy and zinc phosphate (Zn·Ph) conversion coatings are often introduced into the intermediate layers as a post-treatment of the steel surfaces [1].

Accordingly, the emphasis of our present study was directed towards investigating the effect of poly(acrylic acid), p(AA)-modified Zn·Ph coatings on the cathodic delamination of high-temperature performance PPS and PEEK topcoatings in an NaCl solution. Also, we emphasized the exploration of the

changes in chemistry and morphology occurring at the interfaces between PPS or PEEK coatings and phosphated steels after heating-cooling fatigue tests of defect-free polyaryl topcoat/Zn·Ph/steel in an accelerated corrosion environment at 25 to 200°C.

3. Synthesis and Characteristics of Organometallic Polymer Coating Films

Current and pending environmental, health and occupational safety regulations impose serious constraints in industries producing corrosion protective coatings. One such example is the requirement that all paints and binders containing >250 g/l of volatile organic compound (VOC) emissions be removed from the market [17]. In addition, chromium and lead compounds are environmentally hazardous, and pressures to eliminate their use in corrosion barriers for metals and as fillers and pigments in paints are growing. As a result, more effective and environmentally benign corrosion protective coating systems for steel and lightweight metals such as aluminum and magnesium are needed.

With the object of developing environmentally safe coating systems, the pre-ceramic organometallic polymers (OMP) have been investigated for use as corrosion-protective coatings on aluminum (Al) and steel substrates. Some OMP's in terms of the organometallosiloxane polymer (OMSP) were synthesized through a hydrolysis-polycondensation-pyrolysis reaction route of sol precursor solutions consisting of monomeric organofunctional silane, metal alkoxides, $M(OR)_n$, (where M is Ti, Zr, Ge, or Al; R is CH_3 , C_2H_5 , or C_3H_7 ; and n is 2, 3, or 4), methanol, water, and mineral or organic acid as a hydrolysis accelerator [18-20]. Since a sol is a fluid colloidal solution, the addition of HCl as mineral acid produced a clear sol, thereby helping to form smooth, uniform coatings. The formation of this clear sol was due mainly to HCl-catalyzed hydrolysis of monomeric organosilane and $M(OR)_n$. This hydrolysis transformed the organosilanol compounds containing Cl-substituted end groups, and also the hydroxylated metal compounds. In the second part of the reaction stage, dehydrochlorinating and dehydrating polycondensations occurring between these hydrolysates led to the conversion of the sol into a gel. As described by several investigators [21-23], the microstructure of the film can be altered by varying the rate of polymerization of sol particles; namely, the extent of growth of the polymeric sol in an aqueous medium depends primarily on the pH of the precursor solution. When acid-type

catalysts were added to the solution, the sol consisted of entangled linear polymers. By contrast, a highly condensed sol consisting of randomly branched chains was prepared by incorporating base-type catalysts. Xerogel films derived from the acidic sol precursor system had a continuous, dense microstructure, while the base-type system resulted in the formation of globular structures consisting of aggregations of randomly grown individual clusters. Pyrolytic treatment of the OMSP gels, as a final stage, induces the formation of OMSP network structures, while volatilizing the carbonaceous species and eliminating Cl-related by-products from the gel compounds.

Based upon the above information, the emphasis of our present study was directed toward evaluating various OMSP coatings derived from two-step, acid-base-catalyzed sol precursors as protective coatings of Al. The six different OMSPs, polytitanosiloxane (PTS), polyzirconosiloxane (PZS), polyborosiloxane (PBS), polyaluminosiloxane (PAS), polylanthanosiloxane (PLS), and polytinsiloxane (PTIS) were synthesized from sol precursors consisting of N-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole (TSPI) as the monomeric organofunctional silane, $\text{Ti}(\text{OC}_2\text{H}_5)_4$, $\text{Zr}(\text{OC}_3\text{H}_7)_4$, $\text{B}(\text{OCH}_3)_2$, $\text{Al}(\text{OC}_3\text{H}_7)_3$, $\text{La}(\text{OC}_3\text{H}_7)_3$, and $\text{Sn}(\text{OC}_2\text{H}_5)_2$ as $\text{M}(\text{OR})_n$ reactants, methanol, and water over a pH range of 7.1 to 7.9.

As part of our research on the design and fabrication of sol gel-derived OMSP coating films, we also explored the use of monomeric β -trimethoxysilylethyl-2-pyridine, and of bis-cyclopentadienyl zirconium dichloride (zirconocene dichloride) as the metal-containing moiety. The polymerized phase of monomeric organosilane can be classified as a polysiloxane with pendent pyridine groups. Carraher et al., [24,25] have synthesized the titanium, zirconium, and tin-containing polyesters and polyethers in accordance with the Lewis acid-base concept, where the Cl in the metallocene dichlorides (Cp_2MCl_2 , where M is metal) is the electrophilicity, and the amine, carboxylate, thiol, or hydroxyl groups present in the organic species, as opposed to Cp_2MCl_2 , were the nucleophilicities. They also reported that the presence of metallocene moiety in the polymer structure conferred better weatherability to exterior coatings by retarding ultraviolet-associated degradations because of its ability to absorb UV radiation. Therefore, we judged that it would be valuable to synthesize pyridine-pendant polysiloxane polymers containing a backbone modified with metallocene moiety for use as sol-precursor-derived thin coating films. The sol

precursors of this OMSP family, in terms of the polymetalloenesiloxane-2-pyridine, were prepared by incorporating the hydrolysate formed by in the mineral acid-catalyzed hydrolysis of β -trimethoxysilylethyl-2-pyridine in the liquor solution into the zirconocene dichloride (Cp_2ZrCl_2) dissolved in tetrahydrofuran as the organic solvent.

On the other hand, the polysilazanes (PSZ) were synthesized over forty years ago [26,27], they have not been subject to extensive research, and the applications of PSZ are only in the initial stages [28]. Recently, attention was given to using PSZ as coatings [29,30], in applications where polymers are often employed as protective and reinforcement materials for metallic and ceramic substrates. Lenhart, et al., [29] reported that PSZs have a high potential for use as high-temperature performance coatings of aluminum alloys. Thus, our particular interest was to evaluate the ability of PSZ to protect steel substrates from corrosion. Since the conformational changes in PSZ are temperature dependent, it is important to identify the best chemical conformation of PSZ coatings which provide a barrier to corrosion.

Accordingly, our attention was focused on understanding and elucidating the physico-chemical factors that provide OMSP and PSZ coatings with good or poor protective properties.

4. Organic Polymer Coatings by Flame Spray Technology

The use of anticorrosion thermoplastic coatings applied by flame spray technology is of increasing interest encompassing a wide variety of applications including rail cars, solvent tanks, pipes, valves, and bridges [31-33]. Attention has focused on this technology because it solves the limitation of conventional liquid-applied coatings using a hot oven and dipping tank which must be large enough to accommodate the material to be soaked.

In flame spraying, the powdered thermoplastics are conveyed by compressed air to a hand-held applicator gun and then the powder is melted as it passes through the propane flame. Subsequently, the melted polymers are accelerated onto the substrate at a high velocity ($50\text{-}100\text{ ms}^{-1}$). The simplicity of the process allows the coating to be applied in the field, which is very cost effective. In addition, there are no limitations on shelf- or pot-life.

When polyethylene $\text{-(CH}_2\text{-CH}_2\text{)-}_n$ (PE) thermoplastic polymers were considered for use as coatings to protect metals against corrosion, considerable

attention was paid to their poor adherence to the metal substrates, primarily due to the lack of functional groups, such as -OH, C=O and COOH, in the PE structure. One effective way to circumvent this problem is to incorporate methacrylic acid [$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{OOH}$] (MA) into the PE.

Based upon this information, this work explores how flame spray MA-modified PE coatings adhere to cold rolled steel surface and investigates how the structure of interfacial bonds between the modified PE and the steel act to retard or accelerate the rate of corrosion of the steels.

SUMMARY AND RESULTS

1. Surface Modification of Electrogalvanized Steels

The surfaces of electrogalvanized steels (EGS) were modified to inhibit NaCl corrosion of Zn layers and to improve their paint-adhesion properties by immersing EGS panels into Co-incorporated zinc phosphating solutions consisting of $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, H_3PO_4 , poly(acrylic acid)[p(AA)], $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and water at 80°C . The electrochemical reaction between Co dissociated from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Zn in the acid media created short-circuited cells by the flow of electrons from Zn acting as the anode to Co as the cathode. Such a cathodic activity increasingly promotes the anodic dissolution of Zn, $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$, and is reflected by a brisker evolution of hydrogen from the Co. Similar cathodic activity was also observed from the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Considering the precipitation of crystalline zinc phosphate tetrahydrate (hopeite) on the EGS surface, a high degree of ejection of Zn ions contributed significantly to the rapid growth of hopeite crystals deposited on EGS. Uniform hopeite layers completely converting over the EGS surfaces were observed on the specimens prepared by immersion for only 5 sec, thereby conferring good protection layers against corrosion. Thus, it is apparent that the service life of Zn layers as protective barriers for underlying steels could be extended. On the other hand, EGS surfaces having poor adherence to polymeric topcoats were transformed into chemically and physically reactive surfaces by depositing hopeite. The great improvement of bond strength between hopeite and the polyurethane (PU) topcoat was due mainly to the following two factors; 1) the interfacial chemical reaction between p(AA) at the outermost surface sites of hopeite layers and PU, and 2) the mechanical interlocking bonds caused by the anchoring effects of PU penetrating into the rough hopeite layers.

Although Co, Ni, and Cr have a great effect on creating numerous cathodic reaction sites over the zinc surfaces, these transition metals are known to be environmentally hazardous materials. Thus, additional work to find replacements for environmentally benign transition metals, such as Mn, Fe, Zr, Ti, et al., will be needed.

2. High-Protective Performance Polyaryl Coating Systems

To enhance the performance of high-temperature polyphenylene sulfide (PPS) and poly(phenyl ether ether ketone) (PEEK) coatings in protecting steels from

corrosion, the cold-rolled steel surfaces were prepared with zinc phosphate (Zn•Ph) conversion coatings as an interfacial tailoring material. The ability of these coating systems to protect the steel against corrosion was evaluated in terms of the rate of cathodic delamination of the coating layer from the steel. Because the cathodic reaction, $\text{H}_2\text{O} + 1/2\text{O}_2 + 2\text{e}^- = 2\text{OH}^-$, at the corrosion side of a defect in the coating layer creates a high pH environment at the interfacial boundary between the coating and steel, the magnitude of susceptibility of the interfacial intermediate layers to the alkali-induced degradation played a key role in suppressing cathodic failure. For the PPS coating systems, this cathodic delamination was due mainly to alkali-induced dissolution of Zn•Ph layers. However, the rate of delamination for the PPS/Zn•Ph systems was considerably lower, compared with that for the PPS/steel system in the absence of Zn•Ph. The lowest level was observed in the N_2 -induced PEEK/Zn•Ph/steel joint systems, thereby decreasing the rate of delamination. By contrast, oxidized PEEK induced by air in same joint systems was susceptible to the alkali-catalyzed hydrolysis. This phenomenon significantly promoted the alkali dissolution of Zn•Ph crystals, reflecting a high rate of delamination. Nevertheless, the introduction of Zn•Ph as interfacial tailoring material into the intermediate layers markedly acted in reducing the cathodic delamination of PPS or PEEK/steel joint systems.

To evaluate the ability of PEEK and PPS thermoplastic coatings to protect zinc phosphate (Zn•Ph)-treated steels from corrosion in a wet, harsh environment (1.0 wt% H_2SO_4 , 3.0 wt% NaCl and 96.0 wt% water at temperatures from 25° to 200°C), we exposed them in autoclave to attempt heating-cooling cyclic fatigue tests (1 cycle = 12 hr at 200°C + 12 hr at 25°C) up to 90 times. Although no changes in appearance were seen in the PEEK specimens after 60 cycles, extending the cycles to 90 caused the delamination of the coating film from the Zn•Ph. The major reason for this delamination was the degradation of the PEEK polymer caused by its hydrothermal-catalyzed esterification. In the PPS-coating systems, the major chemical reaction at the interfaces between the PPS and Zn in the Zn•Ph layer during cycling led to the formation of ZnS reaction product, which enhanced the Zn•Ph-to-PPS adhesive bond; correspondingly, there were no signs of peeling and separation of the coating after 90 cycles. In addition, because these intermediate reaction products are insoluble at high pH, they minimized the rate of delamination of the PPS coating caused by the cathodic reaction, $\text{H}_2\text{O} + 1/2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$, at the corrosion side of a defect in the film. In contrast, PEEK

coatings containing non-reactive Zn•Ph underwent cathodic delamination, because of the susceptibility of Zn•Ph to alkali dissolution. Thus, we believe that combined layers of PPS and Zn•Ph provide great protection to steels in a harsh environment with temperatures up to 200°C.

Because these polyaryl polymers are thermoplastic, their drawback in applying as the high-temperature performance coating materials is to have a limited temperature; namely, if the surrounding temperature was > melting points ($\approx 300^\circ\text{C}$), it is impossible for them to protect the metals. To solve the drawback of such thermoplastic coatings, the development of the thermosetting polymer coating systems with a high glass transition point of $> 300^\circ\text{C}$ will be needed as the additional work.

3. Synthesis and Characteristics of Organometallic Polymer Coating Films

Various organometallosiloxane polymers (POMSs), such as polytitanosiloxane (PTS), polyzirconosiloxane (PZS), polyborosiloxane (PBS), polyaluminosiloxane (PAS), polylanthanosiloxane (PLS), and polytinsiloxane (PTIS) were synthesized through the hydrolysis-polycondensation-pyrolysis route of two-step, acid-base catalyzed sol precursors consisting of N-[3-(triethoxysilyl)propyl-4,5-dihydroimidazole (TSPI) as monomeric organofunctional silane, metal alkoxides, $\text{M}(\text{OR})_n$ [M: Ti, Zr, B, Al, La, and Sn, R: CH_3 , C_2H_5 , and C_3H_7 , n: 2, 3, or 4], methanol, and water, at pHs from 7.1 to 7.9. The synthesized OMSPs were then evaluated as corrosion-protective coatings of aluminum (Al) substrates. The OMSP-coated Al specimens were prepared by dipping the alkali-etched Al into the sol precursor solutions, then pre-heated at 100°C to form xerogel films. Subsequently, xerogel-coating films were pyrolyzed in air at 300°C for 30 min.

A microstructural geometry of 300°C -treated OMSP coating surfaces, in which fractal clusters were linked together, was characteristic of PTS, PZS, PAS, and PTIS coatings, while no fractal features were seen on the PBS and PLS coatings. The surface microstructure for the latter films showed a wrinkled and grained texture caused by thermal shrinkage of film and the formation of oxidized particles in the film layers, respectively.

Considering the way in which Al is attacked by chloride, corrosion will occur in the following ways. The adsorption of Cl^- on the Al oxide and hydroxide surfaces results in the formation of water-soluble Al chloride complex ions, such as AlCl_2^+ and AlCl_4^- , thereby promoting the diffusion of Al^{3+} ions and e^- electrons

through the oxide film at the anodic reaction sites. Since OH^- ions are generated by cathodic reaction of atmospheric reactants such as O_2 and H_2O , with the e^- from the anode, ($2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-$), the corrosion reaction between Al^{3+} , Cl^- , and OH^- ions, ($\text{Al}^{3+} + 2\text{Cl}^- + 2\text{OH}^- \rightarrow \text{Al}(\text{OH})_2\text{Cl}_2^-$), leads to the formation of transitory colloidal complexes which attenuate the oxide film. Once the passivating Al_2O_3 layer becomes sufficiently thinned, metallic Al reacts directly with the electrolyte to cause pitting corrosion. The adsorption of Cl^- appears to be a preliminary step in the formation of a corrosion pit [34].

The following four factors played an essential role in improving the protective ability of OMSP coatings on Al substrates; 1) the increase in densification of M-O-Si linkages in the OMSP network structure with an increased treatment temperature from 100° to 300°C, 2) the minimum susceptibility of film surfaces to water-wetting behavior, 3) the interlocking morphology between cluster units consisting of symmetrical fractal branches, and 4) the dense microstructure of clusters of $\approx 2 \mu\text{m}$ entirely covering the metal substrate. The major contribution of factors (3) and (4) was to minimize the stress generated by the shrinkage of films, so that there was no crazing nor peeling. Polytitanosiloxane (PTS) was identified as the most effective cluster-coating film which exhibited all of these important factors. For example, PTS had an impedance of $> 10^6 \text{ ohm-cm}^2$ after a 40-day exposure to a 0.5 N NaCl solution at 25°C, a 3000-hr salt-spray resistance, and a grate protection at both anodic (inhibits pitting) and cathodic sites. The extent of such resistance to corrosion was far better than that of conventional anodic oxide and Cr-conversion coatings. Hence, PTS coating has a high potential as substitutive materials for the Cr-incorporated coatings which are known to be environmentally hazardous.

On the other hand, the pyridine-pendent siloxane polymers containing backbone modified with zirconocene (Cp_2Zr) moiety in terms of the polyzirconocenesiloxane-2-pyridine (PZSP) were synthesized through the hydrolysis-condensation reaction generated by mixing solutions of two phases; one was a sol solution, consisting of β -trimethoxysilylethyl-2-pyridine (TSEP), water, CH_3OH , and HCl , and the other was zirconocene dichloride (Cp_2ZrCl_2) dissolved in tetrahydrofuran. The synthesized PZSP polymers were then evaluated for use as thin coating film systems fabricated by a simple dip-withdrawing method. The following five factors, 1) wettability of the Al surface by the mixing solution, 2) susceptibility of the film surfaces to moisture, 3) molecular

conformation of the polymers, 4) film-forming performance, and 5) the chemical state at interfaces between PZSP and Al, played an important role in ensuring that the coatings appropriately protect Al alloys against NaCl-associated corrosion. Referring to 1), the surface tension of film-forming solution decreased with increasing amounts of Cp_2ZrCl_2 added to TSEP, thereby resulting in a good wetting performance. The factors 2) to 4) depended primarily on the proportions of TSEP sol to Cp_2ZrCl_2 solution, and the curing temperatures; the surfaces of coating film derived from an proper TSEP/ Cp_2ZrCl_2 ratio at 150°C had a low susceptibility to moisture. The reason for their lesser sensitivity was due to the formation of Si-O- Cp_2Zr linkages generated by dehydrating condensation between the silanol end groups in siloxane and the hydroxyl groups in $\text{Cp}_2\text{Zr}(\text{OH})_2$ formed by the hydroxylation of Cp_2ZrCl_2 . However, two critical factors, a low TSEP/ Cp_2ZrCl_2 ratio and an increase in exposure temperature to 200°C , caused the development of stress-microcracks by the shrinkage of film, because of the exceeding densification of Si-O-Si and Si-O-Zr linkages. Relating to the last factor, pyridine nitrogen in PZSP seems to have a certain degree of affinity with the oxygen in Al_2O_3 existing at the outermost surface sites of Al. Such an affinity led to the formation of -N \rightarrow O-Al metal bond structure at the PZSP- Al_2O_3 interfaces, suggesting that the PZSP coatings strongly adhere to the Al surfaces. In other words, this interfacial interaction generates the self-organized molecular structure on the metal surfaces from the randomly oriented molecules of a sol solution.

Consequently, a TSEP/ Cp_2ZrCl_2 ratio of 90/10 was identified as the optimum formulation contributing to the assemblage of uniform, continuous, crack-free coating films over Al. This coating, with thickness of 0.5-1.0 μm , displayed the ability similar to that of PTS coating to protect Al from corrosion.

With regard to the polysilazane (PSZ) coatings, the following generalizations can be drawn from our results. When PSZ is applied as the pre-ceramic-type coating to protect steel against corrosion, the major factors governing the fabrication of a continuous uniform PSZ film over the steel surfaces are 1) the chemical structure of the PSZ, and 2) the film-forming temperatures. In the case of the first factor, the most promising of the coating films was derived from poly(1,1-dimethylsilazane), denoted as PS112. The secondary factor suggested that the conversion of the linear silazans structure in PS112 into crosslinking or cyclic units at temperatures of $\geq 400^\circ\text{C}$ results in

the formation of undesirable films which develop a large number of microcracks in their layers.

Although the 300°C-derived PS112 coating film could protect steels in a NaCl solution against corrosion, the cathodic reaction, $\text{H}_2\text{O} + 1/2\text{O}_2 + 2\text{e}^- = 2\text{OH}^-$, which occur around defects in the covering led to the delamination of the film from the steel. Such cathodic delamination is not only caused by the formation of corrosion products of steel underneath the film, but also to the high susceptibility of PS112 film in the vicinity of steel to alkali-catalyzed hydrolysis. The latter phenomenon was related directly to the formation of water-soluble silanol and NH_3^+ salt compounds as by-products, which were generated by the breakage of Si-C and N-Si bonds in the PS112 structure caused by the attack of OH^- ions.

Although the subject is of ever increasing interest, there are still four major questions to be answered before their effective use as corrosion-protective primers; 1) the role of organometallic polymer (OMP) conformations in transporting ionic and non-ionic corrosive species through the coating film in the corrosion and protection of Al and steel substrates, 2) assuming that the defect of film occurred, the fundamental understanding of the interfacial OMP-anodized or unanodized Al and steel bond structures which serve in sustaining a good performance of adhesion and in providing the self-healing behavior at the corrosion sites, 3) the decomposition mechanisms of films under the corrosion conditions, and 4) the adherent properties of OMP primer surfaces to the polymeric topcoats. The integration of this information will subsequently yield the knowledge of molecular design and tailoring needed for assembling the advanced OMP films which provide a superior protection of Al alloy and steels against corrosion.

4. Organic Polymer Coatings by Flame Spray Technology

The following generalization can conclusively be drawn for the methacrylic acid-modified polyethylene copolymer coatings by flame spray technology.

(1) The bond strength at interfaces between the copolymer coating and the steel substrate depended primarily on the spraying conditions, and involved three major parameters: 1) the propane-gas pressure, 2) the compressed air pressure in the combustion gas; and 3) the traverse speed of the gun.

(2) The reason for the formation of a good interfacial bond during spraying was due to the introduction of functional oxygen species, COOH and C=O , into the

copolymer coating in contact with the substrate, thereby generating the interfacial interaction between such oxidation-induced functional derivatives and steel.

(3) The adhesive nature of the coating applied by spraying with a combination of a low rate of gas flow and a high rate of air flow was poor because of the decomposition of functional oxygen groups caused by an excessive rate of oxidation of the copolymer.

(4) Although the interfacial bond structures played an important role in improving the bond strength, they were vulnerable to the attack of NaOH fluid formed by the charge valance between the OH^- ions from the cathodic reaction, $\text{H}_2\text{O} + 1/2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$, generated at the corrosion side near defects and Na^+ in the NaCl electrolyte, thereby causing cathodic delamination of copolymer film from the steel.

(5) Nevertheless, the rate of cathodic delamination was correlated directly with the bond strength, suggesting that the optimum set of spraying conditions can minimize the rate of delamination.

This information strongly suggested that, concurrent with modifying spray gun, it is possible to coat the high-temperature performance thermoplastic polymers with melting point of $> 300^\circ\text{C}$ over the metal surfaces in the fields. Thus, additional work to continue its development will be directed towards, 1) the efficiency and economic evaluation of modified spray systems for high-temperature polymers, 2) the physico-chemical factors of spray-induced polymer coatings governing the protection of metals against corrosion, and 3) the field application of the developed technologies.

LIST OF PROGRAM PRESENTATIONS, PUBLICATIONS, AND PATENTS

Paper Presented

T. Sugama, Interfaces of High-Protection Performance Polyaryls-Coated Zinc Phosphated Steels. Proceeding of the 1994 Tri-Service Conference on Corrosion, Orlando, FL, June 21-23, 1994.

Published

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Patents

Sugama, T. Sol-Gel Precursor Solutions and Methods for the Fabrication of Polymetallosiloxane Coating Films. U.S. Patent 5,200,237, Apr. 6, 1993.

Sugama, T. Rapid Deposition of Polymer-Modified Zinc Phosphate Conversion Coatings on Galvanized Steels. AUI 93-21 (pending).

Sugama, T. Polyorganometallosiloxane-2- or -4-Pyridine Coatings. AUI 94-19 (pending).

TECHNOLOGY TRANSFER

In the ARO-sponsored program, three technologies were developed at BNL; there were the rapid deposition of zinc phosphate conversion coatings, organometallosiloxane polymer coatings, and self-healing polyphenylenesulfide-zinc phosphate coating systems. To date, the first technology has been transferred to the Palnut Company, recently purchased the TRW Fasteners Division as exclusive license on the automobile fasteners and brackets, and also to the Novamax Technologies Corporation as non-exclusive license on the formulation of zinc phosphate make-up solutions. Furthermore, a non-exclusive licensing agreement regarding a second technology for use as hexavalent chromium-replaced coating systems of aluminum, magnesium, steel and titanium was signed by Utility Metal Research Corp. Lastly, negotiations directed towards transfer of a third technology to the Exergy, Inc. and Long Island Lighting Company for use as corrosion-protective coatings of aluminum- and steel-based heat exchangers are continued by the BNL's Technology Transfer & Licensing Group.

ARMY INTERACTIONS

To help commercialization of the ARO/BNL-developed polyelectrolyte-modified zinc phosphate coatings for military applications, a R&D program entitled "The Environmentally Benign Zinc Phosphate Conversion Coatings" has been commenced on October 1, 1994, under the sponsorship of the U.S. Tank Automotive Command (TACOM, Mr. Carl Handsy), and the U.S. Army Research, Development and Engineering Center (ARDEC, Dr. Robert Katz). In addition, Palnut Company played an active role in the scale-up to demonstrate the responsibility of the process technology developed in this program. The draft of FY 94 Annual Report, as Phase I, was sent to TACOM, ARDEC, and ARO (Dr. R. Reeber).

STUDENTS AND SUMMER HIRES SUPPORTED BY THIS PROJECT

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- Hung, E. Chemistry Dept., Yale U., (1994).
- Lipford, B. Physics Dept., Alabama A&M U. (1994).
- Seeley, M. Chem. Engr. Dept., U. of Wisconsin-Madison (1995).

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- DuVall, J. Science Dept., Green Valley H.S., NV (1994).

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